

Article

Development of Novel High Li-Ion Conductivity Hybrid Electrolytes of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ (LLZSO) for Advanced All-Solid-State Batteries

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Abstract: A lithium superionic conductor of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ that exhibits the highest lithium ionic conductivity among the sulfide electrolytes and the most promising oxide electrolytes, namely, $\text{Li}_{6.6}\text{La}_3\text{Sr}_{0.06}\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$, are successfully synthesized. Novel hybrid electrolytes with a weight ratio of $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ from 1/1 to 1/3 with the higher Li-ion conductivity than that of the pure $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ electrolyte are developed for the fabrication of the advanced all-solid-state Li batteries.

Keywords: all-solid-state Li batteries; $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$; $\text{Li}_{6.6}\text{La}_3\text{Sr}_{0.06}\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$; $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$; hybrid electrolytes of sulfide and oxide



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1. Introduction

All-solid-state battery electrolyte has received increasing attention because of its advantages such as safety (nonexplosive) and excellent electrochemical properties (high conductivity and wide potential window). A lithium superionic conductor of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ that exhibits an extremely high lithium ionic conductivity of 12 mS cm^{-1} at room temperature was first found by Canno et al. [1], which represents the highest conductivity achieved in the sulfide solid electrolyte, exceeding even those of liquid organic electrolytes. On the other hand, Murugan [2] has reported that $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ exhibits the maximum total (bulk + grain boundary) ionic conductivity of $7.7 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C , which represents the highest conductivity achieved in the solid oxide electrolyte. All-solid-state batteries include a metal-anode and solid-state battery with considerable potential improvements in safety and lifetime, as well as higher energy and power densities [3]. Solid-state Li-ion electrolytes (SSEs) are the key materials for the fabrication of next-generation all-solid-state batteries. The lower reactivity of solids compared with liquids leads to expectations of longer lifetimes for solid-state batteries. Inorganic solid electrolytes could support battery operation at low and high temperatures in which conventional liquid electrolytes would freeze, boil, or decompose. A prominent disadvantage of solid-state systems is the reliance of ionic diffusion on the contact of solid particles. Garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has been considered a promising candidate because of its superior chemical and electrochemical stability with air and metallic Li anode. LLZO with the cubic phase exhibits a Li-ion conductivity of two orders of magnitude higher than that of tetragonal LLZO [4,5]. Many metal elements have been employed to stabilize the cubic phase, among which Ga has been found to be effective in enhancing the lithium-ion conductivity [6]. In the present study, A lithium superionic conductor of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ that exhibits the highest lithium ionic conductivity among the sulfide electrolytes and the most promising oxide electrolytes, namely, $\text{Li}_{6.6}\text{La}_3\text{Sr}_{0.06}\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ (LLZSSO) and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ (LLZSO) are successfully synthesized. Novel hybrid electrolytes with a weight ratio of $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ (LLZSO) to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ from 1/1 to 1/3 with a higher Li-ion conductivity than that of the pure

$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ electrolyte are developed for the fabrication of the advanced all-solid-state Li batteries.

2. Experimental Procedure

LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) was synthesized with the starting materials of Li_2S , P_2S_5 , and GeS_2 , which were weighed, mixed in the $\text{Li}_2\text{S}/\text{P}_2\text{S}_5/\text{GeS}_2$ molar ratio of 5/1/1 in an Ar-filled glove box, placed into a stainless-steel pot, and mixed for 30 min using a vibrating mill. The specimens were then pressed into pellets, placed in a quartz tube, and heated under flowing N_2 at a reaction temperature of 550 °C for 8 h in a furnace. After reacting, the tube was slowly cooled to room temperature under the stream of flowing N_2 . The high ionic conductivity and stability were quantified by positive formation energies and challenging synthesis. In the synthesis of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, high Li mobility often seems to occur at the expense of stability.

LLZO, LLZSO, LLZSSO, LLZGO, and LLZBO were prepared through conventional solid-state reactions. Starting materials of Li_2O (purity 99%), SrO , Ga_2O_3 (4 N), Sb_2O_3 (4 N), Bi_2O_3 (4 N), La_2O_3 (Kanto Chemical Co. Tokyo, Japan, $\geq 99.99\%$ purity), and ZrO_2 (Wako, Tokyo, Japan $\geq 99.9\%$ purity) were weighted at the stoichiometric ratio. The mixture was vibration milled for 6 h, followed by calcination at 1100 °C for 12 h. The synthesized products were characterized by XRD (Rigaku Smart Lab, Tokyo, Japan) using $\text{Cu-K}\alpha$ radiation, $\lambda = 1.542 \text{ \AA}$ in the 2θ range of 10–50° at room temperature.

The ionic conductivity measurements of all the solid electrolyte samples were performed by AC electrochemical impedance spectroscopy using a frequency response analyzer (Solartron 1260, AMETEK Scientific Instruments, Oak Ridge, TN, USA) with a frequency range of 0.1 Hz–1 MHz with an applied voltage of 20–100 mV at 295 K. All electrolyte pellets were polished, and Au was applied by coating at both sides of the pellets, or a gold paste was painted onto each side of the sample as a blocking electrode. The pellets (5 mm diameter and about 1 mm thickness) were heated at 583 K for 5 min under an argon atmosphere to obtain dry samples for carrying out the measurements. All the full batteries were evaluated on the LAND CT2001A battery test system. Charge and discharge tests of the all-solid-state batteries were performed with the figuration of Li-In//solid electrolyte/[LiNbO_3 -coated LiCoO_2 +solid electrolyte] and at 295 K.

3. Results and Discussion

A highly pure crystal of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ that exhibits an extremely high lithium ionic conductivity is successfully synthesized and identified by XRD analysis, as shown in Figure 1.

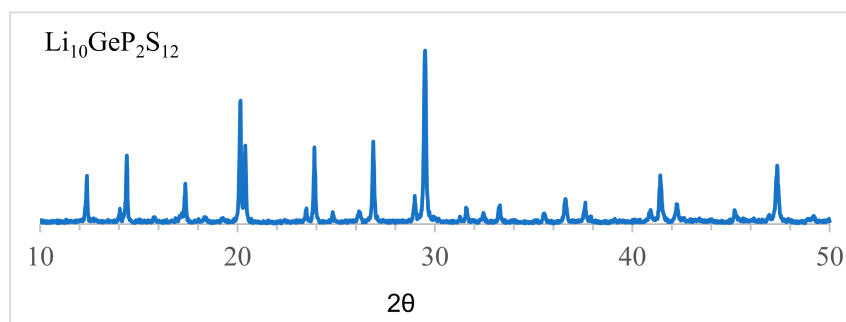


Figure 1. XRD patterns of synthesized $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$.

Li-ion conductivity of synthesized $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte was measured; it is about $1.8 \times 10^{-3} \text{ S/cm}$, as shown in Table 1. The ion conductivity calculation formula is as follows:

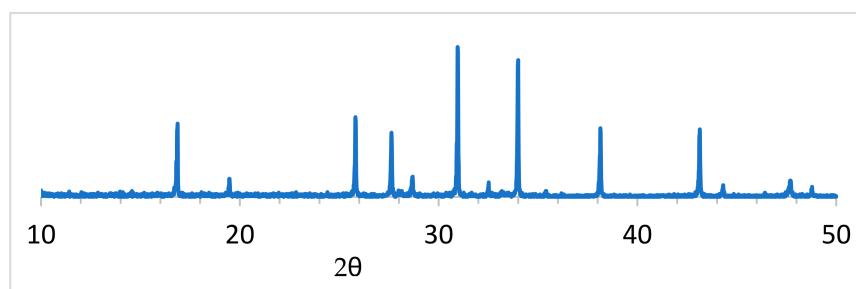
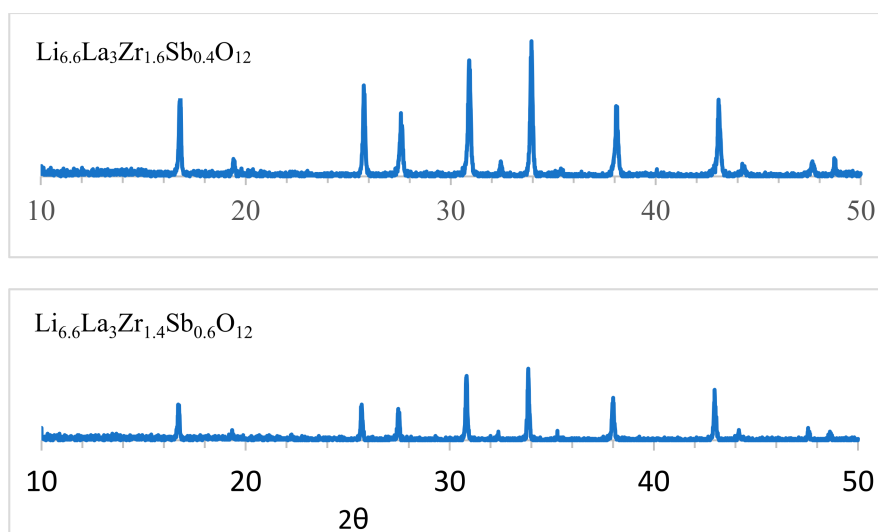
$$\sigma = d/(R \times A)$$

where σ : ion conductivity; d: sample sickness; R: resistance; A: sample area.

Table 1. Li-ion conductivity of synthesized solid electrolytes with different compositions at room temperature (295 K).

Composition	Conductivity σ (S/cm)
$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	1.8×10^{-3}
$\text{Li}_{6.6}\text{La}_{2.94}\text{Sr}_{0.06}\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$	8.5×10^{-4}
$\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$	4.7×10^{-4}
$\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Bi}_{0.4}\text{O}_{12}$	1.3×10^{-4}
$\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Ga}_{0.4}\text{O}_{12}$	1.4×10^{-4}
$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$	9.6×10^{-7}
$\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$	1.3×10^{-5}
$\text{LiGe}_2(\text{PO}_4)_3$	1.1×10^{-7}
LiTa_2PO_8	8.0×10^{-7}
$\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$	6.5×10^{-5}
$\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$	1.0×10^{-5}

The high Li-ion conductivity of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ seems to occur at the expense of stability. The more stable oxide-type electrolytes such as LLZSSO ($\text{Li}_{6.6}\text{La}_{2.94}\text{Zr}_{1.6}\text{Sr}_{0.06}\text{Sb}_{0.4}\text{O}_{12}$) and LLZSO ($\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$) are also successfully synthesized and identified by their XRD patterns, as shown in Figures 2 and 3.

**Figure 2.** XRD patterns of synthesized $\text{Li}_{6.6}\text{La}_{2.94}\text{Zr}_{1.6}\text{Sr}_{0.06}\text{Sb}_{0.4}\text{O}_{12}$.**Figure 3.** XRD patterns of synthesized $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.4}\text{Sb}_{0.6}\text{O}_{12}$.

Li-ion conductivity of synthesized $\text{Li}_{6.6}\text{La}_{2.94}\text{Zr}_{1.6}\text{Sr}_{0.06}\text{Sb}_{0.4}\text{O}_{12}$ and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ solid oxide electrolytes were measured; the Li-ion conductivity of synthesized $\text{Li}_{6.6}\text{La}_{2.94}\text{Zr}_{1.6}\text{Sr}_{0.06}\text{Sb}_{0.4}\text{O}_{12}$ and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ are about 8.5×10^{-4} S/cm and 4.7×10^{-4} S/cm, respectively, at room temperature, as shown in Table 1.

In the oxide electrolyte crystal of LLZSO($\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$), we used Bi and Ga elements instead of Sb to successfully synthesize LLZBO($\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Bi}_{0.4}\text{O}_{12}$) and LLZGO($\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Ga}_{0.4}\text{O}_{12}$) different oxide electrolytes. The XRD patterns of synthesized $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Bi}_{0.4}\text{O}_{12}$ and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Ga}_{0.4}\text{O}_{12}$ are shown in Figure 4. The Li-ion conductivity of synthesized $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Bi}_{0.4}\text{O}_{12}$ and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Ga}_{0.4}\text{O}_{12}$ are about 1.3×10^{-4} S/cm and 1.4×10^{-4} S/cm, respectively, at room temperature, as shown in Table 1. Other oxide electrolytes such as $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$, $\text{LiGe}_2(\text{PO}_4)_3$, LiTa_2PO_8 , $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$, and $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ are also successfully synthesized. The Li-ion conductivity of synthesized $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$, $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$, and $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ are 1.3×10^{-5} S/cm, 6.5×10^{-5} S/cm, and 1.0×10^{-5} S/cm, respectively, at room temperature, as shown in Table 1.

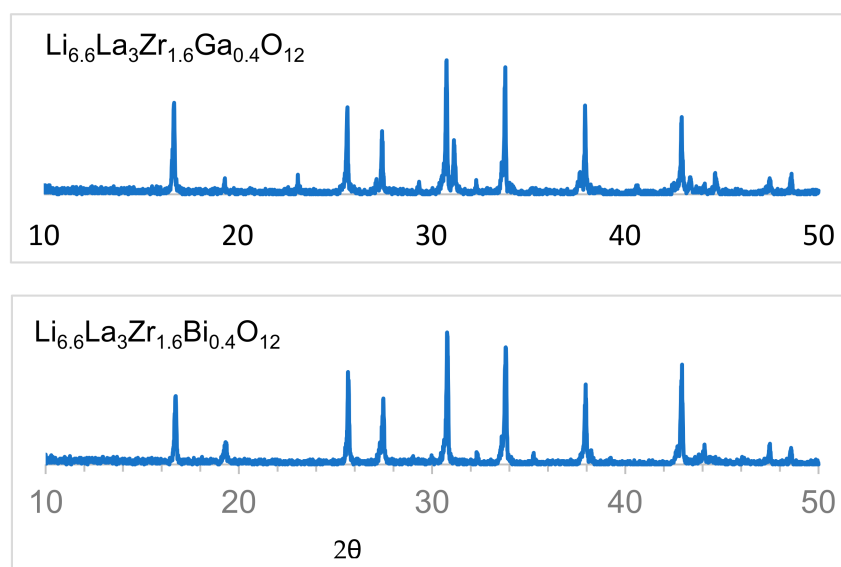


Figure 4. XRD patterns of synthesized $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Ga}_{0.4}\text{O}_{12}$ and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Bi}_{0.4}\text{O}_{12}$.

The Li-ion conductivity of synthesized $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.8}\text{Sb}_{0.2}\text{O}_{12}$, $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$, and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.4}\text{Sb}_{0.6}\text{O}_{12}$ are compared in Table 2. The Li-ion conductivity of synthesized $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.8}\text{Sb}_{0.2}\text{O}_{12}$, $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$, and $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.4}\text{Sb}_{0.6}\text{O}_{12}$ are 2.5×10^{-4} S/cm, 4.7×10^{-4} S/cm, and 3.7×10^{-4} S/cm, respectively, at room temperature, as shown in Table 2.

Table 2. Li-ion conductivity of synthesized LLZSO type solid electrolytes with different compositions at room temperature (295 K).

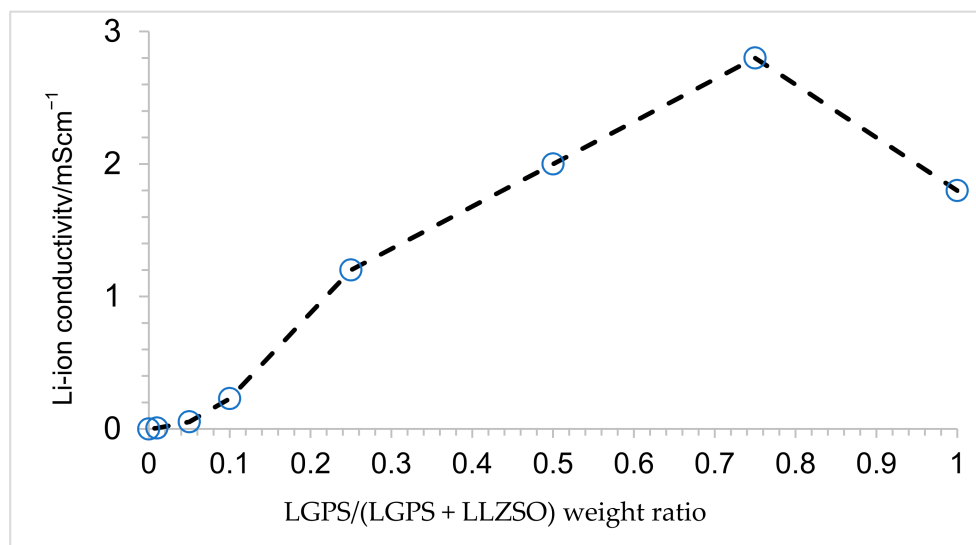
Composition	Conductivity σ (S/cm)
$\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.8}\text{Sb}_{0.2}\text{O}_{12}$	2.5×10^{-4}
$\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$	4.7×10^{-4}
$\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.4}\text{Sb}_{0.6}\text{O}_{12}$	3.7×10^{-4}

To develop the novel solid electrolyte with high Li-ion conductivity and the higher stability, the hybrid electrolytes of LGPS and LLZSO were prepared by mechanically mixing LGPS with LLZSO at the different weight ratio of $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ to $\text{Li}_{10}\text{GeP}_2\text{S}$. The Li-ion conductivity of the prepared hybrid electrolytes of LGPS and LLZSO with different compositions at room temperature (295 K) are listed in Table 3.

Table 3. Li-ion conductivity of hybrid electrolytes of LGPS and LLZSO with different compositions at room temperature (295 K).

Weight Ratio of $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	Conductivity σ (S/cm)
0/1	1.8×10^{-3}
1/3	2.8×10^{-3}
1/1	2.0×10^{-3}
3/1	1.2×10^{-3}
10/1	2.3×10^{-4}
20/1	5.4×10^{-5}
100/1	7.2×10^{-6}

The Li-ion conductivity of hybrid solid electrolytes of sulfide (LGPS) and oxide (LLZSO) as a function of LGPS/(LGPS + LLZSO) ratio at room temperature (295 K) is shown in Figure 5. It has been accepted that the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ is the highest Li-ion conductivity so far. We can infer from Table 3 and Figure 5 that the Li-ion conductivity of hybrid electrolytes with a weight ratio of $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ from 1/1 to 1/3 is higher than the pure LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) electrolyte. It is of significance that the novel hybrid electrolytes with a weight ratio of $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ from 1/1 to 1/3 exhibit a higher Li-ion conductivity than the pure LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) electrolyte.

**Figure 5.** Li-ion conductivity of hybrid solid electrolytes of sulfide (LGPS) and oxide (LLZSO) as a function of LGPS/(LGPS + LLZSO) ratio at room temperature (295 K).

The pure solid oxide electrolytes and pure solid sulfide electrolytes have been extensively studied. However, the novel solid hybrid electrolytes of oxide (LLZSO) and sulfide (LGPS) are first reported in the present paper, which opens a door for developing the more advanced hybrid solid electrolytes different from pure oxides and sulfides. Further studies on the mechanism of the high-ion conductivity of the novel hybrid electrolytes and the characterization of the hybrid electrolytes will be conducted in our future research.

4. Conclusions

Novel hybrid electrolytes with a weight ratio of $\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$ to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ from 1/1 to 1/3 with the higher Li-ion conductivity than that of the pure $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ electrolyte are found for the fabrication of advanced all-solid-state Li batteries.

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References

1. Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; et al. A lithium superionic conductor. *Nat. Mater.* **2011**, *10*, 682–686. [[CrossRef](#)] [[PubMed](#)]
2. Ramakumar, S.; Satyanarayana, L.; Sunkara, V.; Manorama, S.V.; Murugan, R. Structure and Li⁺ dynamics of Sb-doped Li₇La₃Zr₂O₁₂ fast lithium ion conductors. *Chem. Chem. Phys.* **2013**, *15*, 11327–11338. [[CrossRef](#)] [[PubMed](#)]
3. Placke, T.; Klopsch, R.; Dühnen, S.; Winter, M. Lithium ion, lithium metal, and alternative rechargeable battery technologies: The odyssey for high energy density. *J. Solid State Electrochem.* **2017**, *21*, 1939–1964. [[CrossRef](#)]
4. Inoue, T.; Mukai, K. Are all-solid-state lithium-ion batteries really safe?—verification by differential scanning calorimetry with an all-inclusive microcell. *ACS Appl. Mater. Interfaces* **2017**, *9*, 1507–1515. [[CrossRef](#)] [[PubMed](#)]
5. Bartsch, T.; Strauss, F.; Hatsukade, T.; Schiele, A.; Kim, A.Y.; Hartmann, P.; Janek, J.; Brezesinski, T. Gas evolution in all-solid-state battery cells. *ACS Energy Lett.* **2018**, *3*, 2539–2543. [[CrossRef](#)]
6. Kuhn, A.; Gerbig, O.; Zhu, C.; Falkenberg, F.; Maier, J.; Lotsch, B.V. A new ultrafast superionic Li-conductor: Ion dynamics in Li₁₁Si₂PS₁₂ and comparison with other tetragonal LGPS-type electrolytes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14669–14674. [[CrossRef](#)] [[PubMed](#)]